

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : <b>A61K 7/075</b>		A1	(11) International Publication Number: <b>WO 95/01153</b> (43) International Publication Date: <b>12 January 1995 (12.01.95)</b>
(21) International Application Number: <b>PCT/SE94/00632</b> (22) International Filing Date: <b>23 June 1994 (23.06.94)</b>		(81) Designated States: <b>FL JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>	
(30) Priority Data: <b>9302263-0 30 June 1993 (30.06.93) SE</b>		Published <i>With international search report.</i>	
(71) Applicant <i>(for all designated States except US)</i> : <b>BEROL NOBEL AB [SE/SE]; S-444 85 Stenungsund (SE).</b>			
(72) Inventors; and (75) Inventors/Applicants <i>(for US only)</i> : <b>PALICKA, Jadwiga [SE/SE]; Ekbackevägen 26, S-181 46 Lidingö (SE). POOL, Hazel [GB/GB]; Suite 4.5 HPA, Litchurch Plaza, Litchurch Lane, Derby DE2 8AA (GB).</b>			
(74) Agent: <b>ANDERSSON, Rolf; Berol Nobel AB, S-444 85 Stenungsund (SE).</b>			

(54) Title: **SHAMPOO COMPOSITIONS**

(57) Abstract

Shampoo compositions comprising three components, namely at least one amphoteric compound, of the alkylaminopolyamphocarboxyglycinate type, a mixture of two monoethanol amides and an anionic surfactant. Optionally there also may be other amphoteric present.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Bein	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**SHAMPOO COMPOSITIONS**

The present invention relates to shampoo compositions with good foam building properties, providing body for the hair, silky feel to the hair and very good hair combing properties.

Shampoo compositions providing conditioning to the hair are already known and are described in the art of shampoo formulating. Conventional conditioning agents currently used are e.g. cationic surfactants and cationic polymers. Some of these cationic materials cannot in general be used with cleaning anionic surfactants and still deliver satisfactory hair conditioning. Another problem is that the normally compatible types of conditioners, the cationic polymers, may cause so called "build-up" on the hair after repeated usage, which may result in lank or greasy hair.

In EP-A2-152194 a conditioning shampoo is disclosed containing a quaternary ammonium or imidazolinium compound in conjunction with higher alkylamido betaines as amphoteric surfactants and aminofunctional silicones. The latter are said to improve properties such as dry combing and body of the hair.

A hair conditioning composition is disclosed in the Swedish patent application 8004858-0, wherein the conditioning is provided by the combination of a cationic polymer and an amphoteric surfactant forming a conditioning complex on the hair. This complex is said to have the advantage of being retained on the hair even after several washes.

EP-A3-160507 relates to a conditioning shampoo which avoids a problem arising from the presence of the conventional conditioning agents in shampoo formulations. By the frequent use of these shampoo formulations the substantivity of the conditioning agent on the hair leads to a build up of the same, making the hair go greasy more quickly. The shampoo of the patent solves this problem by providing a shampoo free from the traditional conditioners but comprising at least two

amphoteric surfactants, the first being a non-irritant cleaner and the second primarily acting as a conditioner. The shampoo also optionally contains an anionic surfactant.

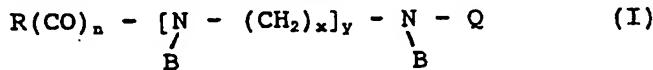
Furthermore, shampoo compositions like those disclosed in EP-A3-160507, may often contain viscosity builders and foaming agents, such as diethanol amides of fatty acids like coconut diethanol amide. However, one drawback of this type of diethanol amides are that they contain small amounts, e.g. 140 to 2000 ppb (part per billion), of nitroso compounds, a highly undesirable contaminant.

EP-A2-214868 and WO 92/05236 disclose a cleaning composition and a dishwashing composition, respectively. These compositions contain at least one amphoteric compound and at least one anionic compound. Furthermore, they may contain lauryl diethanol amide or an amine oxide as a foaming agent.

The shampoo compositions of the present invention provide a conditioning benefit to the hair, resulting in body for the hair with silky feel and very good combing properties, without any build up of conditioning agent on the surface of the hair. They also provide good foam building properties and suitable viscosity building with a negligible level of nitroso contaminants.

The present shampoo compositions comprise three essential components, namely at least one amphoteric compound being of the alkylaminopolyamphocarboxyglycinate type, a mixture of two monoethanol amides and an anionic surfactant. Optionally there may also be other amphoteric present, chosen from the groups as defined below.

The amphoteric compound which is present in the composition is of the alkylaminopolyamphocarboxyglycinate type of the general formula



wherein

R is a hydrocarbyl group of from 7 to 22 carbon atoms,  
n is 0 or 1,

x is 2 or 3,

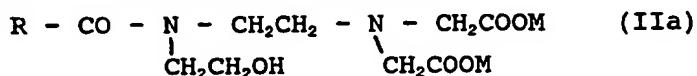
y is an integer of 0 to 4, preferably from 2 to 3,

Q is  $\text{CH}_2\text{COOM}$  or  $\text{CH}_2\text{CH}_2\text{COOM}$ , wherein M is hydrogen or a monovalent cation, such as alkali metals, ammonium or substituted ammonium, and

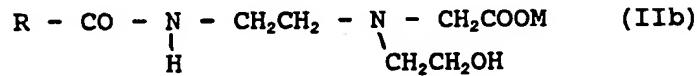
B is hydrogen or a group Q as defined.

This amphoteric is mainly used as a lather former and cleaning agent. It also reduces the irritation from irritating anionic surfactants which are normally always included in shampoo formulations. One example of it is the commercially available Ampholak 7CX/C, sold by Berol Nobel AB, Sweden. In this product R=coco alkyl; n=0, x=y=3 and Q=B=C<sub>2</sub>H<sub>4</sub>COONa. Another example is Ampholak X07, sold by Berol Nobel AB, Sweden. In this product R=rapeseed alkyl; n=0; x=y=3 and Q=B=C<sub>2</sub>H<sub>4</sub>COONa

The optional amphotericics which can be present, are preferably of two different types, the first one being a mixture of the general formulae



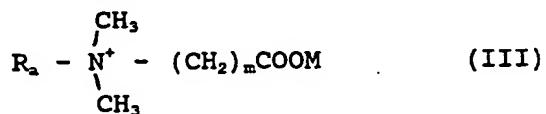
and



wherein R and M have the same meanings as defined above.

The weight by weight ratio of the compound of (IIa) to that of (IIb) in the mixture is within the range of 1:10 to 10:1, preferably within the range of 1:5 to 5:1. The main purpose of this mixture is the use as a hydrotrope and solubilizer. An example of it is the commercially available Ampholak XCO-30, sold by Berol Nobel AB, Sweden. In this product mixture R=coco alkyl and M=Na.

The second type of optional amphoteric is chosen among the betaines with the general formula



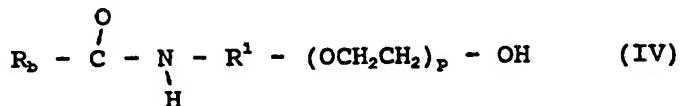
wherein

$R_a$  is a hydrocarbyl chain of 7-21 carbon atoms and preferably is an alkyl or alkenyl radical of from 11 to 17 carbon atoms;  $m$  is 1 or 2; and

$M$  is preferably H or a monovalent cation, such as sodium ion.

5 An example is Amphoteen® 24, commercially available from Berol Nobel AB, Sweden. In this product  $R_a$ =Coco alkyl,  $m=1$ , and  $M=Na$ .

10 The second essential component of the shampoo composition is a mixture of two different monoethanol amides in a weight by weight ratio of 1:10 to 10:1, preferably 1:4 to 4:1, of the general formula



15 wherein

$R^1$  is an alkyl group with 2 to 4 carbon atoms;

$p$  is an integer of from 0 to 10, preferably from 0 to 4, and most preferably from 1 to 4; and

20  $R_b$  represents a fatty acid radical (aliphatic group such as saturated and unsaturated alkyl groups) with 9 to 23 carbon atoms derived from a vegetable oil, preferably rapeseed oil and coconut oil.

25 In a preferred blend 10-90%, preferably 40-80% by weight are amides, where  $R_b$  has from 9-14 carbon atoms, and 10-90, preferably 20-60% by weight are amides where  $R_b$  has from 15-23 carbon atoms. Examples of suitable blends are blends between coconut fatty acid monoethanol amides and rapeseed fatty acid monoethanol amides including ethoxylates thereof in a weight ratio of 1:10 to 10:1, preferably in a weight ratio of 1:4 to 4:1. Besides the viscosity building 30 activity the mixture of monoethanol amides has a foam stabilizing and foam boosting activity.

35 Anionic surfactants suitable for inclusion in the compositions are those generally used in personal care products and include alkylsulfates, ethoxylated alkyl sulfates, alkyl polyglucoside sulfates, fatty acid polyglyceride sulfates, fatty acylamido polyoxyethylene sulfate, alkyl glyceryl ether

5 sulfonates, methyl acyl taurates, fatty acyl glycimates, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl phosphate esters, ethoxylated alkyl phosphate esters, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. The alkyl and/or acyl groups for these surfactants contain 8-22, preferably 10-18 carbon atoms.

10 Preferred from the viewpoint of optimum performance alkyl ether sulphates and alcohol sulphates, especially the salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol with 10-18 carbon atoms and from about 1 to about 5 moles of ethylene oxide, with sodium, ammonium or magnesium being the preferred counterions. One 15 preferred anionic surfactant is sodium lauryl ether sulphate with two ethyleneoxy units. The anionic surfactants act as foam builders and cleansing agents.

20 In addition to the above components other optional ingredients may also be included in the present compositions, such as preservatives, pearlescent agents, colourants and fragrance.

25 Preservatives may e.g. include Euxyl K 100 (Schülke and Mayr), benzyl alcohol, methylchloroisothiazolinone and methylisothiazolinone. The pearlescent agent may e.g. be Empicol XP40 (Albright & Wilson). The colourants may e.g. include FDC Yellow and FDC Orange 4.

30 The pH of the composition should be within a range of 5.0 to 7.0, and preferably 5.5. A pH adjusting agent can be used, such as an organic acid, e.g. citric or lactic acid, or an inorganic acid, e.g. hydrochloric acid.

35 The shampoo compositions of the invention comprise: 10-60%, preferably 15-35%, of the amphoteric component; 5-40%, preferably 10-25%, of the blend of monoethanol amides; and 15-85%, preferably 35-65%, of the anionic surfactant, by weight of the total of these three components.

35 The invention is illustrated by means of the following examples.

**Example 1**

Two different shampoo compositions according to the invention were prepared containing the ingredients as set forth in Table 1.

5

**Table 1**

		Composition 1	Composition 2
	Anionic sulphate	27.5%	25.0%
	Ampholak 7CX/C	10.0%	-
	Ampholak MSX-2		10.0%
10	Amide CMA/2	3.0%	2.0%
	Amide RMA/2	1.0%	1.0%
	Empicol XP40	5.0%	5.0%
	Preservative (Euxyl K100)	0.1%	0.1%
	Perfume (Duffi 0/662601 ex Dragoco)	0.1%	0.1%
15	FDC Yellow 5	0.00025%	-
	FDC Orange 4	-	0.00025%
	Demineralized Water	Balance	Balance
	Citric Acid	qs	qs
20		100.0%	100.0%

20

Anionic surfactant: Sodium lauryl di(oxyethylene) sulphate  
Ampholak MSX-2: Blend of amphoteric

Ampholak 7CX/C 45%, Amphoteen 24 35%, Ampholak XCO-30 20%

Amide CMA/2 = Coco monoethanol amide 2EO

25

Amide RMA/2 = Rapeseed monoethanol amide 2EO

In the compositions 1 and 2 a level of 3-8 ppb for the nitroso contaminant has been found, which is negligible.

To evaluate compositions 1 and 2, a so called "half head" testing method was used. With the half head test, shampoos can be tested and compared in pairs. A single head of hair is washed using two products, one on each half. This allows direct performance comparisons to be made. Several parameters are assessed, e.g. volume and texture of foam, wet and dry feel, etc. Each one is given a score. The results are

30

then calculated and presented as graphs or in tables.

For comparison a leading UK conditioning shampoo (Timotej) was tested in the same manner. The results from two test series using 5 and 20 heads respectively gave in all respect a similar or improved performance for the inventive products in comparison with the commercial shampoo. The inventive shampoos showed excellent conditioning properties with a silky afterfeel, a good wet feel and rinseability among other things without the inclusion of any traditional (polymeric) type of conditioning additives.

**Example 2**

The compositions in Table 2 below were prepared.

**Table 2**

	Compounds	Compositions, % by weight				
		1	2	A	B	C
15	Compound with formula I R=coco alkyl; n=0; x=y=3 B=Q=C <sub>2</sub> H <sub>4</sub> COONa	10		10	10	10
20	Compound with formula I R=rapeseed alkyl; n=0; x=y=3; B=Q=C <sub>2</sub> H <sub>4</sub> COONa		10			
	Lauryl-2EO-sulphate	27.5	27.5	25.5	27.5	27.5
25	Pearlescent agent	5	5	5	5	5
	Coco alkyl monoethanol amide + 2EO	3	3	4	-	-
30	Rapeseed alkyl mono- ethanol amide + 2EO	1	1	-	4	-
	Dimethyl amino oxide	-	-	-	-	4
35	Water	rest	rest	rest	rest	rest

The pH-value of the compositions were adjusted to 5.5 and then tested with regard to the viscosity at 20°C in accordance with Höppler; the foam volume stability measured 5 as the difference in foam volume with and without sebum (1 g/l) after 5 minutes in accordance with Wilmsmann; and the lather drainage stability measured as the difference in lather drainage after 5 minutes with and without sebum (1 g/l) in accordance with Wilmsmann. The following results were 10 obtained.

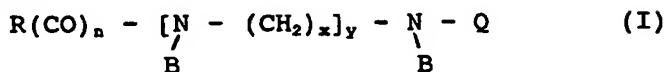
Table 3

Properties	Compositions				
	1	2	A	B	C
Viscosity, cP	6300	8100	3900	solid	4800
Foam volume stability, ml	10	100	260	170	240
Lather drainage stability, s	11	8	47	73	60

From the result it is evident that the composition in accordance with the invention has a viscosity that makes them suitable to be used in shampoo compositions. Furthermore, the foam volume and lather drainage created are unusually 20 stable and are comparatively unaffected on the presence of greasy materials like sebum.

## CLAIMS

1. Shampoo composition comprising
  - (i) (a) at least one amphoteric compound of the general formula



wherein

R is a hydrocarbyl group of from 7 to 22 carbon atoms,

10            n is 0 or 1,

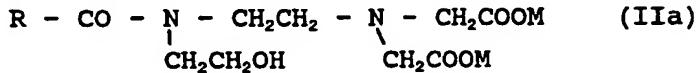
x is 2 or 3,

y is an integer of 0 to 4, preferably from 2 to 3,

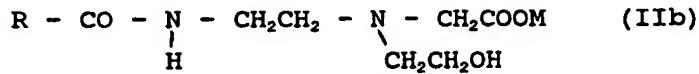
Q is  $\text{CH}_2\text{COOM}$  or  $\text{CH}_2\text{CH}_2\text{COOM}$ , wherein M is hydrogen or a monovalent cation, and

15 B is hydrogen or a group Q as defined.

(b) an amphoteric substance comprising a mixture of the general formulae

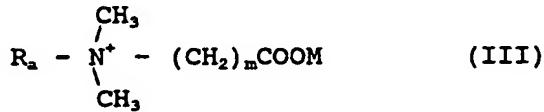


20 and



wherein R and M have the same meanings as defined above;  
and/or

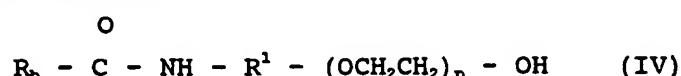
25 (c) an amphoteric compound of the general formula



wherein

30  $R_a$  is a hydrocarbyl chain of 7-21 carbon atoms and preferably is an alkyl or alkenyl radical of from 11 to 17 carbon atoms;  $m$  is 1 or 2; and  $M$  has the same meaning as above.

35 (ii) a mixture of two different monoethanol amides of the  
general formula



wherein

$R^1$  is an alkyl group with 2 to 4 carbon atoms;  
p is an integer of from 0 to 10, preferably from 0 to 4, and  
most preferably from 1 to 4; and

5  $R_b$  represents a fatty acid radical with 9 to 23 carbon atoms  
derived from a vegetable oil; and  
(iii) one or more anionic surfactants;  
comprising 10-60%, preferably 15-35%, of the amphoteric  
component; 5-40%, preferably 10-25%, of the blend of  
10 monoethanol amides; and 15-85%, preferably 35-65%, of the  
anionic surfactant, by weight of the total of these three  
components.

2. A composition according to claim 1 comprising from 15  
to 35% of the amphoteric component, from 10 to 25% of the  
15 monoethanol amides and from 35 to 65% of the anionic  
surfactant, by weight of the total of these three components.

3. A composition according to claim 1 or 2 wherein the  
monoethanol amides are composed of a mixture of coconut  
fatty acid monoethanol amide and rapeseed fatty acid  
20 monoethanol amide in a weight by weight ratio of 1:10 to  
10:1.

4. A composition according to claim 3, wherein said weight  
ratio is from 1:4 to 4:1.

5. A composition according to claim 1, 2, 3 or 4  
25 containing an alkanolamide blend where 40-80% of the  
alkanolamides have a  $R_b$  group having 9-14 carbon atoms and  
20-60% by weight of the alkanolamides have a  $R_b$  group having  
15-23 carbon atoms.

6. A composition according to any of the preceding claims  
30 wherein the weight ratio of the amphoteric compounds of the  
formulae (IIa) and (IIb) is within the range of 1:10 to 10:1.

7. A composition according to claim 6 wherein said ratio  
is within the range of 1:5 to 5:1.

8. A composition according to any of the preceding claims  
35 wherein the anionic surfactant is chosen from the group of  
alkyl ether sulfates and alcohol sulfates.

11

9. A composition according to claim 8 wherein the anionic surfactant is sodium lauryl ether sulfate 2 EO.
10. A composition according to any of the preceding claims wherein the pH is between 5.0 to 7.0.

5

## INTERNATIONAL SEARCH REPORT

International application No. PCT/SE 94/00632
--

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: A61K 7/075

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA, WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0160507 (FISHLOCK-LOMAX, ERIC GRAHAM), 6 November 1985 (06.11.85) --	1-10
A	EP, A2, 0214868 (AMPHOTERIC INTERNATIONAL LIMITED), 18 March 1987 (18.03.87), page 2, line 11 - line 15, line 20 - line 32; page 3, line 9 - line 18, line 25; page 4, line 7 - line 8 --	1-10
A	WO, A1, 9205236 (BEROL NOBEL AB), 2 April 1992 (02.04.92), the claims; page 2, line 13 - line 20; page 5, line 1 - line 17; page 6, line 6 - line 7, line 21; page 7, line 5 - line 9, line 16 - line 18 --	1-10

 Further documents are listed in the continuation of Box C. See patent family annex.

- \* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search  26 Sept 1994	Date of mailing of the international search report  12 -10- 1994
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer  Gerd Strandell Telephone No. + 46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

International application No. PCT/SE 94/00632
--

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	COSMETICS SCIENCE AND TECHNOLOGY, Volume 2, second edition, 1972, Ed. M. S. BALSAM et al: "Wiley-Interscience", page 97  --	1-10
A	US, A, 3964500 (R. DRAKOFF), 22 June 1976 (22.06.76), column 10, line 15 - line 35; column 14, line 64  --	1-10
A	EP, A2, 0180464 (DOW CORNING CORPORATION), 7 May 1986 (07.05.86), page 15, line 31 - page 16, line 8; page 16, line 16 - line 17  -----	1-10

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

27/08/94

International application No.	
PCT/SE 94/00632	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0160507	06/11/85	SE-T3- AU-B- AU-A- CA-A- US-A-	0160507 581431 4169085 1261275 4946136	23/02/89 31/10/85 26/09/89 07/08/90
EP-A2- 0214868	18/03/87	SE-T3- DE-A- US-A-	0214868 3686381 4769169	17/09/92 06/09/88
WO-A1- 9205236	02/04/92	AU-A- EP-A- JP-T-	7903291 0500819 5502265	15/04/92 02/09/92 22/04/93
US-A- 3964500	22/06/76	NONE		
EP-A2- 0180464	07/05/86	AU-B- AU-A- CA-A- JP-C- JP-B- JP-A- US-A-	578497 4921685 1259262 1657273 3021523 61109707 4559227	27/10/88 08/05/86 12/09/89 13/04/92 22/03/91 28/05/86 17/12/85